

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-077071

(43)Date of publication of application : 14.03.2000

(51)Int.Cl.

H01M 4/58
H01M 4/02
H01M 10/40

(21)Application number : 10-241918

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(22)Date of filing : 27.08.1998

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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance battery characteristics, especially charge/discharge cycle characteristics, storage characteristics, and safety.

SOLUTION: A positive electrode of a nonaqueous electrolyte secondary battery contains (A) a lithium manganese composite oxide and (B1) lithium nickel composite oxide with specific surface area X $0.3 \leq X$ (m²/g), preferably $X \leq 3.0$ (m²/g) or (B2) a lithium nickel composite oxide with D50 particle size ≤ 40 μ m.

LEGAL STATUS

[Date of request for examination] 27.08.1998

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3024636

[Date of registration] 21.01.2000

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a nonaqueous electrolyte rechargeable battery. Furthermore, it is concerned with a detail at a lithium secondary battery or a rechargeable lithium-ion battery, and is related with the nonaqueous electrolyte rechargeable battery which is high capacity and has improved a charge-and-discharge property, especially hot a cycle life, and a capacity preservation property and self-discharge nature.

[0002]

[Description of the Prior Art] A manganic acid lithium is an ingredient which attracts expectation very much as one of the positive-electrode ingredients for rechargeable lithium-ion batteries. Although this ingredient system is already reported as a candidate for research of magnetic behavior in the 1950s (Journal of American Chemical Society Vol.78, pp 3255-3260) It will be Material in 1983. Research Bulletin Vol.18 It has reported that M.M.Thackeray and others can take Li ion in and out electrochemically in pp 461-472. Since, The examination as a positive-electrode ingredient of a lithium secondary battery has been made. (For example) Journal of Electrochemical Society Vol.136 No.11 pp 3169-3174 or Journal of Electrochemical Society Vol.138 No.10 pp 2859-2864.

[0003] This manganic acid lithium takes the Spinel structure expressed with a chemical formula LiMn_2O_4 , is between presentations with $\lambda\text{-MnO}_2$, and functions as a 4V class positive-electrode ingredient. Since the manganic acid lithium of Spinel structure has the host structure of a different three dimension from the layer structure which LiCoO_2 grade has, most geometric capacity is usable and excelling in a cycle property is expected.

[0004] However, when the lithium secondary battery which used the manganic acid lithium for the positive electrode in fact repeated charge and discharge, capacity degradation to which capacity falls gradually was not avoided, but the big problem was left behind to the utilization.

[0005] Then, various approaches are examined in order to raise the cycle property of an organic electrolytic-solution rechargeable battery of having used the manganic acid lithium for the positive electrode. for example, the property improvement (JP,3-67464,A --) by improving the reactivity at the time of composition JP,3-119656,A, JP,3-127453,A, JP,7-245106,A, the property improvement (JP,4-198028,A --) by controlling an indication and particle size to JP,7-73883,A etc. Although an indication, the property improvement (it indicates to JP,5-21063,A etc.) by removing an impurity, etc. are mentioned to JP,5-28307,A, JP,6-295724,A, JP,7-97216,A, etc. The improvement in the cycle property that all are satisfying is not attained.

[0006] Apart from the above, the attempt which aimed at improvement in a cycle property is also made by making the presentation ratio of Li sufficiently superfluous to stoichiometry by JP,2-270268,A. It is indicated by JP,4-123769,A, JP,4-147573,A, JP,5-205744,A, JP,7-282798,A, etc. about composition of the same superfluous Li presentation multiple oxide. The improvement in the cycle property by this technique can be checked experimentally and clearly.

[0007] moreover -- as what aimed at effectiveness similar to overLi presentation -- Mn spinel ingredient LiMn_2O_4 and this ingredient -- Li -- rich Li-Mn multiple oxide $\text{Li}_2\text{Mn}_2\text{O}_4$ -- the technique which is made to mix O_4 , LiMnO_2 , and Li_2MnO_3 grade, and is used as positive active material is also indicated by JP,6-338320,A, JP,7-262984,A, etc. however, another Li in adding Li superfluously -- in order that charge-and-discharge capacity value and a charge and discharge energy value might decrease while a cycle property improves if it is made to mix with a rich compound, there was a problem which cannot reconcile a high energy consistency and a long cycle life. on the other hand -- JP,6-275276,A -- a high energy consistency and a high -- although the attempt which aims at improvement in a rate charge-and-discharge property (the current in the case of charge and discharge is large to capacity) and the integrity of a reaction, and enlarges specific surface area is made, achievement of a high cycle life is conversely difficult.

[0008] Examination which aims at improvement in a property has also been performed by on the other hand adding another element to the compound of three components of Li-Mn-O. For example, they are addition and dopes, such as Co, nickel, Fe, Cr, or aluminum, (it indicates to JP,4-141954,A, JP,4-160758,A, JP,4-169076,A, JP,4-237970,A, JP,4-282560,A, JP,4-289662,A, JP,5-28991,A, JP,7-14572,A, etc.). These metallic element addition still needs to be devised, in order to be satisfied as total engine performance with reduction of charge-and-discharge capacity.

[0009] In examination of other element addition, the improvement of other properties, for example, a cycle property, and a self-discharge property is expected, without hardly accompanying boron addition by reduction of charge-and-discharge capacity. For example, that is indicated by JP,2-253560,A, JP,3-297058,A, and JP,9-115515,A. All are immersed in the water solution of a boron compound (for example, boric acid), solid phase mixing, or a boron compound in a manganese dioxide or a lithium manganese multiple oxide, and the multiple oxide of lithium manganese boron is compounded by heat-treating. Since surface activity was reducing the complex particle powder of these boron compounds and manganic acid ghosts, it was expected that a reaction with the electrolytic solution would be controlled and the preservation property of capacity would be improved.

[0010] However, only by boron addition, grain growth, reduction of tap density, etc. arose and it did not link with high capacity-ization as a cell directly. Moreover, depending on synthetic conditions, the capacity fall in the effectual potential range at the time of combination with a carbon negative electrode was seen, or reaction control with the electrolytic solution was sometimes inadequate, and effectiveness was not necessarily in the improvement of a preservation property.

[0011] Although various approaches have been tried by the cycle property improvement of a manganic acid lithium as mentioned above, since a degradation device is promoted, under current, the cycle property which is equal to Co system in use, especially the elevated-temperature operating environment, implementation of the cycle property in elevated-temperature use is asked for the further device. If a notebook computer, an electric vehicle, etc. consider the breadth of a future applicable field, it can especially be said that the cycle property reservation in an elevated temperature is increasing importance.

[0012]

[Problem(s) to be Solved by the Invention] As stated above, the manganic acid lithium LiMn_2O_4 had a problem by two points, that implementation of (1) high-energy consistency (high charge-and-discharge capacity) and coexistence of a high cycle life are difficult for the cell using conventional LiMn_2O_4 , and reduction of the preservation capacity by current (2) self-discharge, although it was the multiple oxide which attracts the great expectation as alternate material of the mainstream positive active material LiCoO_2 .

[0013] Although affinity with the technical problem and the technical electrolytic solution of cell manufacture etc. is pointed out as this cause, the following [pay / to what is depended on the effect of the positive-electrode ingredient itself and a positive-electrode ingredient reason / one's attention] can be considered.

[0014] As a cause by which a high energy consistency is unrealizable probably, the effect of the superfluous imbalance of the ununiformity of a reaction, separation of a phase, and the presentation ratio of Li and Mn and an impurity, lack of tap density, etc. are mentioned.

[0015] Although it depends for the ununiformity of a reaction, and separation of a phase on a synthetic process, in the case of the process calcinated after dry blending, it is mainly determined by mixed homogeneity, and the particle size and burning temperature of a start raw material. namely, -- since a reaction advances on a solid phase front face, if burning temperature is too high in mixing of the source of Li and the source of Mn being inadequate, or particle size being too coarse -- Mn_2O_3 and Mn_3O_4 and Li_2O -- a phase like Mn_2O_3 , LiMnO_2 , $\text{Li}_2\text{Mn}_2\text{O}_4$, $\text{Li}_2\text{Mn}_4\text{O}_9$, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ is generated, and the fall of cell voltage and the fall of energy density are caused.

[0016] The cause of capacity degradation accompanying a charge-and-discharge cycle is in the impedance rise in which the elution or Mn elution of Mn from that the average valence of Mn ion changes between trivalent and tetravalence as charge compensation accompanying receipts and payments of Li, therefore Jahn-Teller distortion arises during a crystal and a manganic acid lithium originates. That is, as a cause of capacity degradation that charge-and-discharge capacity falls, inactivation by the deposit of a up to [the elution of Mn from the effect of an impurity and a manganic acid lithium and the negative-electrode active material of eluted Mn, or a separator] and isolation of an active material particle, the effect of the acid further generated with content moisture, degradation of the electrolytic solution by the oxygen emission from a manganic acid lithium, etc. can be considered by repeating a charge-and-discharge cycle.

[0017] When the single spinel phase is formed, become the form which Mn tends to dissolve into the electrolytic solution when trivalent Mn in Spinel structure dismutates the elution of Mn in part to tetravalent Mn and divalent Mn, While it is possible to be eluted from relative lack of Li ion etc. and generating of an irreversible capacitive component and turbulence of the atomic arrangement under crystal are promoted by the

repeat of charge and discharge Eluted Mn ion deposits on a negative electrode or a separator, and is considered to bar migration of Li ion. Moreover, when a manganic acid lithium takes Li ion in and out, cubic symmetry is accompanied by distortion, and several% of expansion and contraction of unit-lattice length according to the Jahn-Teller effectiveness. Therefore, by repeating a cycle, electric poor contact arises in part, or it is expected that the particle which separated also stops functioning as an electrode active material.

[0018] It is thought that emission of the oxygen from a manganic acid lithium furthermore also becomes easy along with Mn elution. In accordance with a cycle, 3.3V plateau capacity becomes large and, as for the manganic acid lithium with many oxygen defects, a cycle property also deteriorates as a result. Moreover, if there is much emission of oxygen, it will be surmised that disassembly of the electrolytic solution is affected, and it is thought that cycle degradation by degradation of the electrolytic solution is also caused. Although an improvement of a synthetic approach, other transition-metals element addition, overLi presentation, etc. have so far been considered for solution of this trouble, it has come to satisfy reservation of high discharge capacity, and both sides of a high cycle life to coincidence.

[0019] Therefore, reducing Mn elution, mitigating distortion of a grid, lessening an oxygen deficiency, etc. are drawn as a cure.

[0020] Next, if the phenomenon of internal short-circuit, such as lack of alignment of the forward negative electrode of a manufacture process reason of a cell and electrode metal waste mixing, is excepted as a cause of reduction of the preservation capacity by self-discharge, an improvement of a preservation property will also be considered to be [control of the improvement of the stability of a manganic acid lithium to the electrolytic solution, i.e., the elution of Mn, a reaction with the electrolytic solution, emission of oxygen, etc.] effective.

[0021] In the use especially under hot environments, it has been the serious failure of application expansion that these degradation of both is promoted. However, since the ingredient system which can expect the potential with which can be satisfied of engine performance for which a current high performance rechargeable battery is asked, such as the high level of electromotive force, electrical-potential-difference surface smoothness at the time of discharge, a cycle property, and energy density, is restricted, the manganic acid lithium of the new Spinel structure which was excellent in the cycle property without charge-and-discharge capacity degradation and the preservation property is called for.

[0022] By the way, using the mixed oxide of the lithium manganese multiple oxide of LiMn_2O_4 grade and the lithium nickel complex oxide of LiNiO_2 grade as positive active material is indicated by JP,10-112318,A. According to this official report, the irreversible capacity in first time charge and discharge is filled up, and it is supposed that a big charge-and-discharge capacity will be obtained. Moreover, mixing and using $\text{LiCo}_0.5\text{nickel } 0.5\text{O}_2$ for the lithium manganese multiple oxide of LiMn_2O_4 grade as positive active material also at JP,7-235291,A is indicated.

[0023] However, according to examination of this invention person, about a charge-and-discharge property, especially hot a cycle life, and a capacity preservation property and self-discharge nature, the result which should not necessarily be satisfied was not obtained only by using the mixed oxide of a lithium manganese multiple oxide and lithium nickel complex oxide for positive active material.

[0024] Then, this invention is made in view of the above trouble, and aims at offering a cell property especially a charge-and-discharge cycle property, a preservation property, and nonaqueous electrolyte 2 cell that was further excellent in safety.

[0025]

[Means for Solving the Problem] this invention person etc. resulted having very big influence about the improvement of a cycle life [in / in the surface area of the lithium nickel complex oxide to mix, or particle size / a charge-and-discharge property, especially an elevated temperature], and a capacity preservation property and self-discharge nature in a header and this invention, as a result of repeating various examination, in order to attain the above-mentioned purpose.

[0026] That is, this invention relates to a positive-electrode electrode at the nonaqueous electrolyte rechargeable battery characterized by including (A) lithium manganese multiple oxide and the lithium nickel complex oxide whose specific surface area (B1) X is $0.3 \leq X$ (m^2/g).

[0027] Moreover, this invention relates to a positive-electrode electrode at the nonaqueous electrolyte rechargeable battery characterized by including (A) lithium manganese multiple oxide and the lithium nickel complex oxide whose (B-2) D50 particle size is 40 micrometers or less.

[0028] When this invention expresses the weight ratio of said lithium manganese multiple oxide and lithium nickel complex oxide by $[\text{LiMn multiple oxide}]:[\text{LiNi multiple oxide}] = (100-a):a$, it is desirable that it is especially $3 < a \leq 45$.

[0029]

[Embodiment of the Invention] According to examination of this invention person, to the lithium manganese

multiple oxide which is positive active material (B1) When the lithium nickel complex oxide whose specific surface area X is $0.3 \leq X$ (m²/g), or (B-2) D50 particle size mixes and uses the lithium nickel complex oxide which is 40 micrometers or less (1) Mn ion eluted in the electrolytic solution decreased sharply, concentration change of Li ion which exists in coincidence in (2) electrolytic solutions became small, degradation of (3) electrolytic solutions and discoloration were suppressed, and it became clear that generation of an acid is also controlled. The dependency of specific surface area or particle size being still larger in that case is observed extremely.

[0030] Although the mechanism from which such a result is obtained was not necessarily clear, the hydrogen ion (H⁺) generated by the reaction of the moisture and supporting electrolyte which the elution of Mn ion mixed into the electrolytic solution as a large reason in the conventional nonaqueous electrolyte rechargeable battery, this reacted with the lithium manganese multiple oxide, and this invention person presumed that Mn elution happened. As a supporting electrolyte, Mn elution is [that it is especially easy to generate an acid in the case of LiPF₆ or LiBF₄] large. On the other hand, by this invention, it is thought that the above-mentioned predetermined specific surface area or the lithium nickel complex oxide of D50 particle size contained in a positive electrode catches a hydrogen ion. The device which incorporates a hydrogen ion, for example and emits Li ion instead as a reaction at this time is presumed. Moreover, lithium nickel complex oxide may be carrying out a certain work like catalyst poison to the reaction between the 3 persons of a lithium manganese multiple oxide, the electrolytic solution, and water.

[0031] Anyway, in a positive electrode, by making specific lithium nickel complex oxide intermingled, generation of the acid in the electrolytic solution can be controlled, and Mn eluted in the electrolytic solution from lithium manganese multiple oxides, such as a manganic acid lithium, can decrease, and the desorption of the oxygen from lithium manganese multiple oxides, such as a manganic acid lithium, can be similarly decreased with a lithium manganese multiple oxide at coincidence. Therefore, since decomposition and Li concentration change of the electrolytic solution are controlled while structure degradation of the lithium manganese multiple oxide itself is suppressed, the increment in a cell impedance can be prevented. For this reason, a cycle property and a capacity preservation property can be raised. This invention is excellent in the cycle property and the capacity preservation property, even when the supporting electrolyte which is easy to generate an acid like especially LiPF₆ and LiBF₄ is used.

[0032] Furthermore, as lithium nickel complex oxide, when an ingredient system with a bigger charge-and-discharge capacity than a lithium manganese multiple oxide is used, high capacity-ization can also be attained to coincidence as secondary effectiveness.

[0033] further -- this invention -- the mixing ratio of a lithium manganese multiple oxide and lithium nickel complex oxide -- since Mn further eluted in the electrolytic solution from a lithium manganese multiple oxide by making it set to $3 < a$ can be reduced when a rate is expressed with [LiMn multiple oxide]:[LiNi multiple oxide] = $100 - a : a$, a cycle property and a capacity preservation property can be raised. Moreover, generally, lithium nickel complex oxide can obtain the nonaqueous electrolyte rechargeable battery of the very high safety which the lithium manganese multiple oxide originally has by making it set to $a \leq 45$, although it is known that it is inferior to safety compared with a lithium manganese multiple oxide.

[0034] The lithium manganese multiple oxide used for this invention is oxide which consists of a lithium, manganese, and oxygen, and can mention the manganic acid lithium, Li₂Mn₂O₄, and the LiMnO₂ grade of Spinel structure of LiMn₂O₄ grade. as long as the manganic acid lithium of the Spinel structure of LiMn₂O₄ grade is desirable and Spinel structure is taken also in this -- [Li]/[Mn] ratio -- from 0.5 -- shifting -- **** -- as [Li]/[Mn] ratio -- 0.5 to 0.65 -- desirable -- 0.51 to 0.6 -- it is 0.53-0.58 most preferably.

[0035] Moreover, similarly, as long as a manganic acid lithium takes Spinel structure, [Li+Mn]/[O] ratio may shift from 0.75.

[0036] Moreover, when the ease of production and the homogeneity of a cell reaction are taken into consideration, the slurry suitable for the particle size of a lithium manganese multiple oxide producing a positive electrode is weighted mean particle size, and is usually 5-30 micrometers.

[0037] Such a lithium manganese multiple oxide can be manufactured as follows.

[0038] As a manganese (Mn) raw material and a lithium (Li) raw material, first, as a Li raw material, lithium compounds, such as a lithium carbonate, lithium oxide, a lithium nitrate, and a lithium hydroxide, can be used, for example, and manganese compounds, such as manganese salt, such as various Mn oxides, such as electrolytic manganese dioxide (EMD), Mn₂O₃, Mn₃O₄, and a chemistry manganese dioxide (CMD), manganese carbonate, and a manganese oxalate, can be used as a Mn raw material. However, when the ease of reservation of the presentation ratio of Li and Mn, the energy density per unit volume by the difference in bulk density, the ease of the purpose particle-size reservation, the simplicity of the process and handling at the time of carrying out extensive composition industrially, the existence of generating of harmful matter, cost, etc. are

taken into consideration, the combination of electrolytic manganese dioxide and a lithium carbonate is desirable.

[0039] It is desirable to grind a lithium raw material and a manganese raw material as a preceding paragraph story which mixes a start raw material if needed, and to keep step with a suitable particle size. 3-70 micrometers of particle size of Mn raw material are usually 5-30 micrometers preferably. Moreover, 5 micrometers or less of particle size of the source of Li are 10 micrometers or less usually 3 micrometers or less most preferably.

[0040] Since a reaction advances on a solid phase front face, if the generation reaction of a lithium manganese multiple oxide has a too coarse particle size in mixing of the source of Li and the source of Mn being inadequate, a desired presentation and the lithium manganese multiple oxide of structure may not be obtained. For example, in case the manganic acid lithium of Spinel structure is manufactured, when particle size is too coarse, and a phase like Mn_2O_3 , Mn_3O_4 , Li_2MnO_3 , $\text{Li}_2\text{Mn}_4\text{O}_9$, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ may generate, from the manganic acid lithium of Spinel structure, cell voltage may fall or energy density may fall. [that mixing of the source of Li and the source of Mn is inadequate] Therefore, in order to obtain a desired presentation and the lithium manganese multiple oxide of structure, to raise the homogeneity of a reaction and to increase the touch area of a lithium raw material and a manganese raw material, it is desirable to use the above particle size. Then, particle-size control and the granulation of mixed powder may be performed. Moreover, if particle size of a raw material is controlled, the lithium manganese multiple oxide of the purpose particle size can be obtained easily.

[0041] Next, it takes so that the presentation ratio of the lithium manganese multiple oxide with which the mole ratio of Li/Mn targets each raw material may be suited, and it fully mixes, and calcinates in an oxygen ambient atmosphere. Oxygen may use pure oxygen and may be mixed gas with inert gas, such as nitrogen and an argon. The oxygen tension at this time is 50 - 760torr extent.

[0042] Although it is usually 400-1000 degrees C, burning temperature is suitably chosen so that a desired phase may be obtained. For example, a fine-particles consistency may be small in oxygen becoming superfluous relatively, if the phase which will not be made into the purpose of Mn_2O_3 or Li_2MnO_3 grade if burning temperature is too high may carry out generation mixing, cell voltage and energy density may not be enough, although the manganic acid lithium of Spinel structure is manufactured, and burning temperature is too low, and it may not be desirable to implementation of high capacity too. Therefore, 600-900 degrees C is 700-850 degrees C most preferably preferably [although the manganic acid lithium of Spinel structure is manufactured] as a burning temperature.

[0043] Although firing time can be adjusted suitably, it is usually 12 - 48 hours preferably for 6 to 100 hours. Although a cooling rate can be adjusted suitably, it is desirable in the case of the last baking processing to consider as the cooling rate which not to quench is more desirable, for example, is 100-degree-C [/h] or less extent.

[0044] Thus, the fine particles of the obtained lithium manganese multiple oxide are classified further if needed, particle size is arranged, and it mixes with the lithium nickel complex oxide explained below, and uses as positive active material.

[0045] Next, the lithium nickel complex oxide used for this invention is explained. Lithium nickel complex oxide is an oxide which consists of a lithium, nickel, and oxygen, and can mention what doped other elements in part for stabilization, high-capacity-izing, and the improvement in safety to LiNiO_2 , Li_2NiO_2 , LiNi_2O_4 , $\text{Li}_2\text{nickel}_2\text{O}_4$, and these oxides. The oxide which doped other elements, for example to LiNiO_2 as what doped the element besides a part is expressed with $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (it is $0 < x \leq 0.5$), and M is a dope metallic element and expresses one or more kinds of metallic elements chosen from the group which consists of Co, Mn, aluminum, Fe, Cu, and Sr. M may be two or more sorts of dope metallic elements, and the sum of the presentation ratio of a dope metallic element should just be set to x.

[0046] Also in this, LiNiO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ (x is usually 0.1-0.4 in this case.) are desirable.

[0047] In addition, in this invention, the Li/nickel ratio (in $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$, they are Li/[nickel+M] ratio) of the above-mentioned lithium nickel complex oxide may shift from the written stoichiometry somewhat, and the lithium nickel complex oxide of this invention also includes such a case.

[0048] In this invention, as such lithium nickel complex oxide, when specific surface area X uses 0.3 or more, it becomes possible to prevent effectively degradation of a lithium manganese multiple oxide or the electrolytic solution. Moreover, specific surface area is usually 5.0 or less, and since the slurry which can perform electrode spreading easily that it is easy to deal with it in case a positive-electrode electrode is manufactured will be obtained if further 3.0 or less thing is used, it is desirable.

[0049] Moreover, this invention enables it to prevent effectively degradation of a lithium manganese multiple oxide or the electrolytic solution because D50 particle size may use a thing 40 micrometers or less and sets D50 particle size to 40 micrometers or less as the above-mentioned lithium nickel complex oxide. Moreover, D50 particle size is usually 1 micrometers or more, and since the slurry which can perform electrode spreading easily

that it is easy to deal with it in case a positive-electrode electrode is manufactured will be obtained if especially a thing 3 micrometers or more is used, it is desirable.

[0050] In addition, specific surface area expresses the surface area per fine-particles unit weight (m^2/g), and it measures with a gas absorption method by this invention here.

[0051] Moreover, D50 particle size expresses the particle size corresponding to 50% of weight addition values, and it measures with a laser-light-scattering type measuring method.

[0052] Such lithium nickel complex oxide can be manufactured as follows. First, as a lithium raw material, lithium compounds, such as a lithium carbonate, lithium oxide, a lithium nitrate, and a lithium hydroxide, can be used like the above-mentioned. Moreover, nickel hydroxide, nickel oxide, nickel nitrate, etc. can be used as a nickel (nickel) raw material.

[0053] It is desirable to grind a lithium raw material and a nickel raw material if needed, and to arrange and use them for a suitable particle size. In order to obtain a predetermined specific surface area or D50 particle size especially, it is desirable to classify and use the particle size of a nickel raw material.

[0054] Then, after taking so that the presentation ratio of the lithium nickel complex oxide which a Li/nickel ratio makes the purpose may be suited, and mixing enough, it calcinates like manufacture of a lithium manganese multiple oxide. Burning temperature is about 500-900 degrees C. The lithium nickel complex oxide of a desired specific surface area or D50 particle size can be obtained by classifying preferably the lithium nickel complex oxide calcinated and obtained further.

[0055] What mixed such a lithium manganese multiple oxide and lithium nickel complex oxide is used for the positive-electrode electrode used for the nonaqueous electrolyte rechargeable battery of this invention as positive active material.

[0056] In addition, in this invention, the compound generally [LiCoO_2 grade] known as positive active material may be mixed and used as positive active material besides the mixture of such a lithium manganese multiple oxide and lithium nickel complex oxide. Moreover, the quality of an additive for which Li_2CO_3 grade is usually used for safety etc. may be added further.

[0057] As the manufacture approach of a positive electrode, although there is especially no limit, after mixing by the suitable dispersion medium which may dissolve a binder for the fine particles of for example, a lithium manganese multiple oxide, and the fine particles of lithium nickel complex oxide with an electro-conductivity applying agent and a binder (slurry method), and applying it on charge collectors, such as aluminum foil, and it dries a solvent, it is compressed with a press etc. and formed.

[0058] In addition, there is especially no limit as an electro-conductivity applying agent, and things usually used, such as carbon black, acetylene black, a natural graphite, an artificial graphite, and a carbon fiber, can be used. Moreover, what is usually used [polyvinylidene fluoride / (PVDF) / polytetrafluoroethylene (PTFE),] also as a binder can be used.

[0059] On the other hand, as a negative-electrode active material to receive, carbon materials, such as occlusion, graphite which may be emitted, or amorphous carbon, are used for a lithium, a lithium alloy, or a lithium.

[0060] Although especially a separator is not limited, textile fabrics, glass fiber, a porous synthetic-resin coat, etc. can be used. For example, polypropylene and the porous film of a polyethylene system are thin films, and it is suitable in respect of large-area-izing, film reinforcement, or membrane resistance.

[0061] As a solvent of nonaqueous electrolyte, it is usually used well, and can be easy to use carbonate, chlorinated hydrocarbon, ether, ketones, and nitril. Preferably, at least one kind is chosen from diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and ester as a high dielectric constant solvent as at least one kind from ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone (GBL), etc., and a hypoviscosity solvent, and the mixed liquor is used. EC+DEC, PC+DMC, or PC+EMC is desirable.

[0062] As a supporting electrolyte, at least one kind is used from LiClO_4 , LiI , LiPF_6 , LiAlCl_4 , LiBF_4 , $\text{CF}_3\text{SO}_3\text{Li}$, etc. Since effectiveness can be most demonstrated when especially LiPF_6 or LiBF_4 are used, since the acid in the electrolytic solution can be controlled even if it uses the supporting electrolyte which is easy to generate acidity in this invention, it is desirable. The concentration of a supporting electrolyte is 0.8-1.5M.

[0063] As a configuration of a cell, various configurations, such as a square shape, a paper mold, a laminating mold, cylindrical, and a coin mold, are employable. Moreover, what is necessary is not to limit especially these and just to select them according to the above-mentioned configuration, although there are a charge collector, an electric insulating plate, etc. in a component part.

[0064]

[Example] Hereafter, although an example explains this invention further, this invention is not limited to these. In addition, specific surface area is Quanta. Using QuantaSorb by the Chrome company, D50 particle size is Micro. It measured using FRA made from Trac.

[0065] A lithium carbonate (Li_2CO_3) and electrolytic manganese dioxide (EMD) were used for composition of the [example 1 of evaluation trial] manganic acid lithium as a start raw material.

[0066] Grinding of Li_2CO_3 and the classification of EMD were performed for the purpose of obtaining the manganic acid lithium which has reactant improvement and the purpose particle size as a preceding paragraph story of mixing of the above-mentioned start raw material. When using as positive active material of a cell, since the weighted mean particle size of 5-30 micrometers was desirable, the manganic acid lithium also set particle size of EMD to the same 5-30 micrometers as the purpose particle size of a manganic acid lithium by balance, such as homogeneous reservation of a reaction, an ease of slurry production, and safety.

[0067] On the other hand, since the particle size of 5 micrometers or less was desirable for reservation of homogeneous reaction, Li_2CO_3 ground so that D50 particle size might be set to 1.4 micrometers.

[0068] Thus, EMD and Li_2CO_3 which were arranged with a predetermined particle size were mixed so that it might be set to $[\text{Li}]/[\text{Mn}] = 1.05/2$.

[0069] This mixed powder was calcinated at 800 degrees C under the ambient atmosphere of an oxygen flow. Subsequently, the air classifier removed the minute particle with a particle size [in the particle of the obtained manganic acid lithium] of 1 micrometer or less. At this time, the specific surface area of the obtained manganic acid lithium was about 0.9m²/g.

[0070] Moreover, tap density was the fine-particles property that call that 4.09g [// cc] and D50 particle size is 17.2 micrometers, and 2.17g /and true density cc call a lattice constant 8.227Å.

[0071] On the other hand, LiNiO_2 of specific-surface-area of 1.7m²/g was prepared as lithium nickel complex oxide.

[0072] It mixed at a rate of expressing the manganic acid lithium prepared as mentioned above and LiNiO_2 to Table 1, and ten cc of electrolytic solutions of the mixed solvent (50:50 (volume %)) of the propylene carbonate (PC) containing the 5g of mixed powder and LiPF_6 (concentration 1M) and dimethyl carbonate (DMC) was put into the well-closed container.

[0073] These well-closed containers were heated at 80 degrees C, and were left for 20 days. The electrolytic solution was extracted after that and Mn ion concentration in the electrolytic solution was analyzed in ICP. The result is shown in Table 1.

[0074]

[Table 1]

a (LiNiO ₂ 混合比)	電解液中の Mn 濃度
0%	2320ppm
2%	1792ppm
3%	773ppm
5%	623ppm
10%	54ppm
15%	7.5ppm
20%	1.9ppm
30%	<0.2ppm
35%	<0.2ppm

[0075] (the weight of lithium nickel complex oxide when a expresses above and homonymy, i.e., [lithium manganese multiple oxide].: [lithium nickel complex oxide] as :(100-a) a among Table 1 -- a mixing ratio is expressed.)

From this result, Mn eluted in the electrolytic solution decreases, so that LiNiO_2 mixing ratio is high. That is, even if it uses a cell under hot environments, it is expected that the stability of positive active material increases. Although especially the effectiveness of stopping the elution of Mn when LiNiO_2 adds at least in less than 3% of thing is seen, in order to acquire satisfying effectiveness, it is desirable to put in 3% or more. It is 10% or more still more preferably.

[0076] The well-closed container prepared in the example 1 of the [example 2 of evaluation trial] evaluation trial was similarly heated at 80 degrees C, and was left for 20 days. The electrolytic solution was extracted after that and Li ion concentration in the electrolytic solution was analyzed in atomic absorption. The result is shown in Table 2.

[0077]

[Table 2]

a (LiNiO ₂ 混合比)	電解液中の Li 濃度
0%	5577ppm
2%	5617ppm
3%	6323ppm
5%	6364ppm
10%	6402ppm
15%	6418ppm
30%	6420ppm
35%	6422ppm

(表中、a は表 1 と同義である。)

[0078] If based on Li concentration in the electrolytic solution of the mixed solvent (50:50 (volume %)) of the propylene carbonate (PC) containing LiPF₆ (concentration 1M) and dimethyl carbonate (DMC) being about 6400 ppm, LiNiO₂ mixing ratio is 3% or more, and it can be said that Li concentration reduction in the electrolytic solution can be controlled. When 1/3 or less [of Mn concentration when not mixing lithium nickel complex oxide] is made into a standard, a is understood that three or more are desirable also from a viewpoint of Li concentration reduction control in the electrolytic solution.

[0079] As lithium nickel complex oxide, seven kinds of LiNi_{0.8}Co_{0.2}O₂ powder, 3.0m²/g, 2.36m²/g, 1.50m²/g, 0.71m²/g, 0.49m²/g, 0.30m²/g, and 0.25m²/g, was prepared as a specific surface area using the manganic acid lithium compounded like the example 1 of an evaluation trial as a [example 3 of evaluation trial] lithium manganese multiple oxide.

[0080] next, a manganic acid lithium and LiNi_{0.8}Co_{0.2}O₂ of various specific surface area -- predetermined weight -- it mixed with the mixing ratio (a= 0, 3, 5, 10, 15, 20, 30, 35), and ten cc of electrolytic solutions of the mixed solvent (50:50 (volume %)) of the propylene carbonate (PC) containing the 5g of mixed powder and LiPF₆ (concentration 1M) and dimethyl carbonate (DMC) was put into the well-closed container like the example 1 of an evaluation trial.

[0081] These well-closed containers were heated at 80 degrees C, and were left for 20 days. The electrolytic solution was extracted after that and Mn ion concentration in the electrolytic solution was analyzed in ICP. The result is shown in drawing 1 . It turns out that the effectiveness which controls Mn elution is high, so that specific surface area is large.

[0082] In the thing of under 0.3m²/g, the effectiveness of Mn elution control has a too small specific surface area of lithium nickel complex oxide, and if it is not a> 45, it will not become 1/3 or less [of Mn concentration when not mixing lithium nickel complex oxide] from the result of the example 3 of an evaluation trial. therefore, if specific surface area is not a thing more than 0.3m²/g, it turns out that effectiveness sees and is not stopped.

[0083] As lithium nickel complex oxide, six kinds of LiNi_{0.8}Co_{0.2}O₂ powder whose D50 is 2 micrometers, 3 micrometers, 15 micrometers, 26 micrometers, 40 micrometers, and 45 micrometers was prepared using the manganic acid lithium compounded like the example 1 of an evaluation trial as a [example 4 of evaluation trial] lithium manganese multiple oxide.

[0084] next, a manganic acid lithium and LiNi_{0.8}Co_{0.2}O₂ of various specific surface area -- predetermined weight -- it mixed with the mixing ratio (a= 0, 3, 5, 10, 15, 20, 30, 35), and ten cc of electrolytic solutions of the mixed solvent (50:50 (volume %)) of the propylene carbonate (PC) containing the 5g of mixed powder and LiPF₆ (concentration 1M) and dimethyl carbonate (DMC) was put into the well-closed container like the example 1 of an evaluation trial.

[0085] These well-closed containers were heated at 80 degrees C, and were left for 20 days. The electrolytic solution was extracted after that and Mn ion concentration in the electrolytic solution was analyzed in ICP. The result is shown in drawing 2 . It turns out that the effectiveness which controls Mn elution is high, so that particle size is small. moreover, the mixing ratio of larger lithium nickel complex oxide than D50 particle size of 40 micrometers -- alpha -- a> 45 -- even if -- Mn elution volume does not become 1/3 or less [of Mn concentration when not mixing lithium nickel complex oxide]. Therefore, the effectiveness will not be accepted if D50 particle size is not a thing 40 micrometers or less.

[0086] As lithium nickel complex oxide, five kinds of LiNi_{0.8}Co_{0.2}O₂ powder, 4.5m²/g, 3.2m²/g, 3.0m²/g, 1.50m²/g, and 0.30m²/g, was prepared as a specific surface area using the manganic acid lithium compounded like the example 1 of an evaluation trial as a [example 5 of evaluation trial] lithium manganese multiple oxide. Carbon black was blended dryly as a manganic acid lithium, LiNi_{0.8}Co_{0.2}O₂, and an electro-conductivity applying agent, it kneaded [be / it / under / N-methyl-2-pyrrolidone / in which PVDF which is a binder was dissolved / (NMP) / adding], homogeneity was distributed, and the slurry for cells was created. At this time, it is a manganic acid lithium:LiNi_{0.8}Co_{0.2}O₂:electro-conductivity applying agent :P It was the mixing ratio (a=

25) of VDF:NMP=30:10:5:5:50 (% of the weight).

[0087] After measuring with a Brookfield viscometer, and applying the slurry to homogeneity on an aluminum metallic foil with a thickness of 25 micrometers, it considered as the positive-electrode sheet by evaporating NMP. Specific surface area, a slurry, and the condition of spreading are shown in Table 3.

[0088]

[Table 3]

比表面積(m ² /g)	粘度	スラリー状態	電極塗布状態
4.5	22,000	ゲル化した	不可
3.2	18,000	ゲル化した	不可
3.0	6,000	均一に分散	可
1.50	5,000	均一に分散	可
0.30	4,000	均一に分散	可

[0089] From Table 3, since gelation cause electrode spreading becomes difficult when specific surface area is larger than 3.0m²/g, specific surface area is understood that below 3.0m²/g is desirable.

[0090] In the example of the [example 6 of evaluation trial] evaluation trial, it considered as the positive-electrode sheet like the example 5 of an evaluation trial except having prepared LiNi_{0.8}Co_{0.2}O₂ powder whose D50 is 2 micrometers, 3 micrometers, 15 micrometers, 26 micrometers, 40 micrometers, and 45 micrometers as lithium nickel complex oxide. D50 particle size, a slurry, and the condition of spreading are shown in Table 4.

[0091]

[Table 4]

D ₅₀ (μ m)	粘度	スラリー状態	電極塗布状態
2	22,000	ゲル化した	不可
3	8,000	均一に分散	可
15	6,000	均一に分散	可
26	5,000	均一に分散	可
40	4,000	均一に分散	可
45	3,800	均一に分散	可

[0092] Since gelation cause electrode spreading becomes difficult when D50 particle size is smaller than 3 micrometers, Table 4 shows that 3 micrometers or more are desirable as D50 particle size.

[0093] The 2320 coin cel was produced using the manganic acid lithium compounded like the example 1 of an evaluation trial as a [example 7 of evaluation trial] lithium manganese multiple oxide, using LiNi_{0.8}Co_{0.2}O₂ of specific-surface-area of 1.7m²/g as lithium nickel complex oxide.

[0094] That is, the positive electrode rolled out what was kneaded with the mixing ratio (a= 10) of manganic acid lithium:LiNi_{0.8}Co_{0.2}O₂:electro-conductivity applying agent:PTFE=72:8:10:10 (% of the weight) in thickness of 0.5mm, and pierced and produced it by phi12mm. Carbon black was used for the electro-conductivity applying agent here. In the negative electrode, the separator used porous PP film with a thickness of 25 micrometers using phi14mm and the metal Li with a thickness of 1.5mm. The electrolytic solution was used as the mixed solvent (50:50 (volume %)) of the ethylene carbonate (EC) containing LiClO₄ (concentration 1M), and dimethyl carbonate.

[0095] The positive electrode was set to manganic acid lithium:electro-conductivity applying agent:PTFE=80:10:10 (% of the weight) for the comparison with coincidence, and the 2320 coin cel which made a negative electrode, a separator, and the electrolytic solution the same was produced except LiNi_{0.8}Co_{0.2}O₂ not being included.

[0096] The charge-and-discharge cycle trial was performed using these coin cels. A cycle makes charge and discharge the constant current of 0.5 mA/cm², and the charge-and-discharge-voltage range is 3.0-4.5V. vs It carried out by Li. Moreover, evaluation temperature was considered as 10-degree-C unit from 10 degrees C to 60 degrees C.

[0097] The #50-/#1 (discharge capacity of eye 50 cycles to discharge capacity of eye one cycle comparatively) capacity survival rate (%) by the cycle evaluation temperature of the coin cel of the thing (example) containing LiNi_{0.8}Co_{0.2}O₂ and the thing (example of a comparison) which is not included is shown in Table 5. Even if the direction of the coin cel by this invention raises cycle temperature, a capacity survival rate is high.

[0098]

[Table 5]

サイクル評価温度 (℃)	# 50 / # 1 容量残存率 (%)	
	実施例	比較例
10	94	92
20	93	91
30	92	88
40	91	84
50	89	76
60	89	73

[0099] The 18650 cylinder cel was made as an experiment using the manganic acid lithium compounded like the example 1 of an evaluation trial as a [example 8 of evaluation trial] lithium manganese multiple oxide, using $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$ of specific-surface-area of 1.7m²/g as lithium nickel complex oxide.

[0100] That is, carbon black was first blended dryly as a manganic acid lithium, $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$, and an electro-conductivity applying agent, in the N-methyl-2-pyrrolidone (NMP) in which PVDF which is a binder was dissolved, homogeneity was distributed and the slurry was produced. The positive-electrode sheet took after applying the slurry on an aluminum metallic foil with a thickness of 25 micrometers by evaporating NMP. the solid content ratio in a positive electrode -- manganic acid lithium: -- $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$: -- electro-conductivity applying agent :P It was referred to as VDF=72:8:10:10 (% of the weight). At this time, it is a= 10.

[0101] On the other hand, a negative-electrode sheet is carbon :P It mixes and NMP was distributed so that it might become the ratio of VDF=90:10 (% of the weight), and it applied on copper foil with a thickness of 20 micrometers, and produced.

[0102] The electrode sheet of the positive electrode produced as mentioned above and a negative electrode was wound up through the polyethylene porosity film separator with a thickness of 25 micrometers, and it considered as the cylinder cell.

[0103] The electrolytic solution made LiPF_6 of 1M the supporting electrolyte, and the solvent was used as the mixed solvent (50:50 (volume %)) of propylene carbonate (PC) and diethyl carbonate (DEC).

[0104] $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$ is not included in coincidence in a positive electrode for a comparison, but it is a manganic acid lithium:electro-conductivity applying agent about a solid content ratio :P The 18650 cylinder cel was similarly made as an experiment except having been referred to as VDF=80:10:10 (% of the weight).

[0105] The charge-and-discharge cycle trial in 55 degrees C was performed using these cylinder cels. In charge, it went by 500mA to 4.2V, and discharge went by 1000mA to 3.0V. The cycle property comparison of the discharge capacity in 55 degrees C of a cylinder cel is shown about the case (example of a comparison) where it does not contain when $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$ is included in drawing 3 (example). Even if the direction of the cylinder cel by the example of this invention repeats a charge-and-discharge cycle, it turns out that there is little capacity degradation.

[0106] Furthermore, the impedance of each cylinder cel was measured for the charge-and-discharge cycle trial in 55 degrees C by the alternating current impedance method after 100 cycle ***** using the cylinder cel by the above-mentioned example and the example of a comparison. The comparison is shown in drawing 4 . It turns out that the example by this invention of direct-current equivalent resistance and interfacial resistance is also smaller.

[0107] The 18650 cylinder cel was made as an experiment using the manganic acid lithium compounded like the example 1 of an evaluation trial as a [example 9 of evaluation trial] lithium manganese multiple oxide, using $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$ of specific-surface-area of 1.7m²/g as lithium nickel complex oxide.

[0108] The manufacture approach of a 18650 cylinder cel was performed like the example 8 of an evaluation trial.

[0109] At this example of an evaluation trial, the solid content weight ratio in a positive electrode is a manganic acid lithium: $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$:electro-conductivity applying agent :P It examined with the value which shows x (% of the weight) when being referred to as VDF=80-x:x:10:10 in Table 6. In Table 6, a (= x.100/80, above-mentioned a and homonymy) was also written together.

[0110] Thus, the capacity retention test in 55 degrees C was performed using the produced cylinder cel.

[0111] After carrying out constant-current charge of the charge to 4.2V by 500mA, it performed constant-potential charge by 4.2V for 2 hours. Then, the discharge capacity the case where it is made to discharge without placing neglect time amount in a room temperature, and at the time of making it discharge, after leaving it for 28 days in a room temperature was measured. Volumetry set cut-off potential to 3.0V by 500mA under the room temperature environment.

[0112] The rate to the capacity (it is written as 0W capacity) at the time of making it discharge without the

preservation capacity after the neglect during 28 days of the cylinder cel made as an experiment to Table 6 (for it to be written as 4W capacity) and the neglect period of the preservation capacity is shown. When it adds to the case (in the case of $x=0$) where $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$ is not added, after neglect has the high shelf life of capacity for 28 days. Moreover, the capacity of a cylinder cel also increased by the lithium-nickel-complex-oxide mixing effectiveness of high capacity.

[0113]

[Table 6]

x	a	4W 容量 (mAh)	4W 容量/0W 容量 (%)
0	0	1 2 0 5	8 3
4	5	1 3 9 3	9 3
8	1 0	1 4 5 2	9 4
1 2	1 5	1 5 1 1	9 4
1 6	2 0	1 5 5 4	9 5
2 0	2 5	1 5 9 8	9 5
2 4	3 0	1 6 4 2	9 5
2 8	3 5	1 6 8 6	9 5
3 2	4 0	1 7 4 8	9 6
3 5	4 3. 8	1 7 7 4	9 5
3 7	4 6. 3	1 8 1 8	9 5
4 4	5 5	1 8 6 2	9 6
4 8	6 0	1 9 0 6	9 5
5 2	6 5	1 9 4 9	9 5
5 6	7 0	1 9 9 3	9 5

[0114] The safety test was performed using the cylinder cel produced in the example 9 of the [example 10 of evaluation trial] evaluation trial. The result is shown in Table 7. when a manganic acid lithium is used as main positive active material, since safety is high as compared with Co system, it is about the difference in safety on severer conditions in the case -- for the ***** reason, round bar collapse and a pegging test were adopted as a safety evaluation item.

[0115] In the round bar collapse trial, the cell was crushed to 1/2 using the round bar. Moreover, by warning a cell, a pegging test is a trial which makes internal short-circuit cause compulsorily, and the 4mm nail was used for it. All were performed according to UL-1642 for details.

[0116] In the round bar collapse trial, few [x] steams [40 or more] were seen, and it was igniting 52 or more. On the other hand, in the pegging test, when x exceeded 36, emitting smoke was seen, and it was igniting 48 or more. Safety reservation becomes difficult, so that the rate of lithium nickel complex oxide increases.

Therefore, x is set to 36 or less and $a \leq 45$ from a viewpoint of safety.

[0117]

[Table 7]

x	a	丸棒圧壊試験	釘差し試験
0	0	発煙・発火なし	発煙・発火なし
4	5	発煙・発火なし	発煙・発火なし
8	1 0	発煙・発火なし	発煙・発火なし
1 2	1 5	発煙・発火なし	発煙・発火なし
1 6	2 0	発煙・発火なし	発煙・発火なし
2 0	2 5	発煙・発火なし	発煙・発火なし
2 4	3 0	発煙・発火なし	発煙・発火なし
2 8	3 5	発煙・発火なし	発煙・発火なし
3 2	4 0	発煙・発火なし	発煙・発火なし
3 5	4 3. 8	発煙・発火なし	僅かな蒸気
3 7	4 6. 3	僅かな蒸気	発煙
4 4	5 5	僅かな蒸気～発煙	発煙
4 8	6 0	発煙	発火
5 2	6 5	発火	発火
5 6	7 0	発火	発火

[0118] If the result of the above example of an evaluation trial is summarized, as for the lithium nickel complex oxide to mix, $0.3 \leq X \leq 3.0$ (m²/g) is most suitable for specific surface area X from a viewpoint of the viewpoint of Mn elution and the spreading nature of a slurry, and printing nature.

[0119] Moreover, as for the lithium nickel complex oxide to mix, it is most suitable from the viewpoint of the viewpoint of Mn elution and the spreading nature of a slurry, and printing nature that D50 particle size is 3 micrometers or more 40 micrometers or less.

[0120] Moreover, when it is made into [LiMn multiple oxide]:[LiNi multiple oxide] = (100-a):a, as for the ratio of a lithium manganese multiple oxide and lithium nickel complex oxide, $3 < a \leq 45$ is more desirable than the viewpoint of Mn elution, and the viewpoint of safety.

[0121]

[Effect of the Invention] Since Li concentration change in Mn elution from the lithium manganese multiple oxide which is the active material used for nonaqueous electrolyte 2 cell; and the electrolytic solution is controlled according to this invention, nonaqueous electrolyte 2 cell by which the charge-and-discharge cycle, especially the hot charge-and-discharge life have been improved greatly can be offered. Moreover, as for nonaqueous electrolyte 2 cell of this invention, the capacity preservation property is also improved. Furthermore, according to this invention, nonaqueous electrolyte 2 cell excellent also in safety can be offered.

[Translation done.]